Fig. 1. An *ORTEP* (Johnson, 1965) drawing showing the atomic numbering of $C_{25}H_{41}N_2O_2P$; 40% probability level. The H atoms are represented by spheres of arbitrary size.
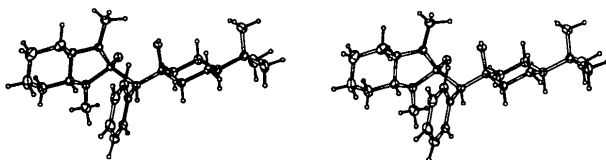

Fig. 2. Stereopair showing the molecular conformation.

moiety. For the other configuration, $R = 0.055$, $wR = 0.047$ and $S = 1.726$. Selected bond distances, bond angles and torsion angles are presented in Table 2.

The programs used here are: modified versions of *NRC*-3, Lp absorption correction; *NRC*-2, data reduction; *NRC*-10, bond distances and angles; and *NRC*-22, mean planes (Ahmed, Hall, Pippy & Huber, 1973); *SHELXS*86 (Sheldrick, 1986); *FORDAP*, Fourier and Patterson maps (A. Zalkin, unpublished); *NUCLS*, least-squares refinement (Doedens & Ibers, 1967); and *ORTEP*, Figs. 1 and 2 (Johnson, 1965).

In the crystal, the molecules are held by hydrogen bonds between O(2)—H(O2) and O(1) where O(2)—

$H(O2) = 0.79$ (3), $H(O2)\cdots O(1^a) = 1.99$ (3), $O(2)\cdots O(1^a) = 2.772$ (4) Å, $O(2)—H(O2)\cdots O(1^a) = 172$ (3)°, and $O(1^a)$ is related to $O(1)$ by $\frac{1}{2} + x$, $\frac{1}{2} - y$, $1 - z$.

Related literature. The anion generated from the phosphonamide (I) showed the same facial selectivity as observed with electrophiles in previous studies by Hanessian, Delorme Beaudoin & Leblanc (1984), Bélanger-Gariépy, Delorme, Hanessian & Brisse (1986), Bélanger-Gariépy, Bennani, Hanessian & Brisse (1989), Bennani, Bélanger-Gariépy & Hanessian (1990), Hanessian, Bennani & Delorme (1990) and Bennani & Hanessian (1991).

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Structure of a Chiral Bicyclic β-Hydroxyphosphonamide – a Product of Kinetic Resolution in an Olefination Reaction, $C_{22}H_{35}N_2O_2P$

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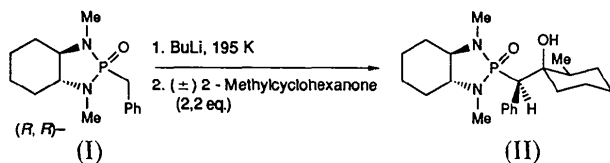**Abstract.** $C_{22}H_{35}N_2O_2P$, $M_r = 390.51$, monoclinic, $P2_1$, $a = 9.101$ (3), $b = 8.612$ (6), $c = 13.790$ (5) Å, $\beta = 92.29$ (3)°, $V = 1080.0$ (9) Å^3, $Z = 2$, $D_x = 1.201$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 0.14$ mm^{-1}, $T = 293$ K, $R = 0.044$, $wR = 0.031$ for 1355 observed reflections. The title compound,

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$C_{22}H_{35}N_2O_2P$

(3aR,7aR)-2-{(R)-α-[(1R,2S)-1-hydroxy-2-methyl-cyclohexyl]phenylmethyl}-1,3-dimethyl-2,3,3a,4,5,6,-7,7a-octahydro-1H-1,3,2λ^5-benzodiazaphosphole 2-oxide, is constituted of a (1R,2R)-N,N'-dimethyl-1,2-diaminocyclohexane group attached to a tetrahedrally coordinated phosphoryl group. A phenylmethyl group with the R configuration bridges the phosphorus atom and a (1R,2S)-1-hydroxy-2-methylcyclohexyl group. The tertiary alcohol is in the axial position and the 2-methyl group is in the equatorial position. An intramolecular hydrogen bond occurs between the phosphoryl group and the hydroxyl group which restricts the conformation. The molecules are held in the crystal by van der Waals interactions.

Experimental. The reaction of the anion formed from the chiral non-racemic bicyclic phosphonamide (I) with (±)-2-methylcyclohexanone under conditions of kinetic resolution gave a crystalline adduct (II) whose structure was elucidated by a single-crystal X-ray diffraction study. This structure unequivocally shows the orientation of the substituents and the equatorial attack of the anion, thus clarifying the proposed pathway of the reaction (Hanessian, Delorme, Beaudoin & Leblanc, 1984).

Crystals of $C_{22}H_{35}N_2O_2P$ bounded by {001}, {01$\bar{1}$} and {101}, dimensions 0.19 × 0.50 × 0.53 mm. Unit cell from 25 well centered reflections in the range 10 ≤ θ ≤ 12°. Nonius CAD-4 diffractometer, graphite-monochromatized Mo $K\bar{\alpha}$ radiation, $\omega/2\theta$ scan technique, $\Delta\omega = (1.00 + 0.35\tan\theta)°$, $2\theta_{max} = 50.0°$ (-10 ≤ h ≤ 10, -10 ≤ k ≤ 10, -16 ≤ l ≤ 0). Orientation monitored every 200 measurements, intensity checked every hour using 6 standard reflections, largest intensity fluctuation ± 1.0%. 2037 unique reflections were collected (4210 measured, averaging

2/m, R_{int} = 0.043) of which 1355, with I ≥ 1.96$\sigma(I)$, were retained for structure determination and refinement. Lp corrections, no absorption correction.

The structure was solved by direct methods (*SHELXS*86)* and difference Fourier syntheses (*SHELX*76). Initial full-matrix least-squares refinement based on F's, block-diagonal approximation in the last cycles, all non-H atoms anisotropic, H atoms initially calculated at idealized positions refined in the last cycles. Enantiomorph imposed from the known chirality of starting material. Function minimized: $\sum w(|F_o| - |F_c|)^2$. Final R = 0.044, wR = 0.031 {weights derived from the counting statistics, $w^{-1} = [\sigma^2(F) + 0.0001(F)^2]$} and S = 1.52 for 384 refined parameters. Max. Δ/σ = 0.53, average Δ/σ = 0.10; in the final difference Fourier synthesis, four peaks of 0.25–0.18 e Å^{-3} at 1.04–1.16 Å from P, general background in the range -0.20, $+0.16$ e Å^{-3}.

The scattering curves for the non-H atoms were taken from Cromer & Mann (1968) and those for the H atoms from Stewart, Davidson & Simpson (1965). Anomalous dispersion of P included, obtained from Cromer & Liberman (1970).

The final coordinates for the non-H atoms are given in Table 1. Selected bond distances and angles including hydrogen-bonding parameters are given in Table 2.† Fig. 1 shows a thermal-ellipsoid plot with the atom numbering.

Related literature. The anion generated from the phosphonamide (I) showed the same facial selectivity

* The programs used here are: modified versions of *NRC*-2, data reduction, *NRC*-10, bond distances and angles and *NRC*-22, mean planes (Ahmed, Hall, Pippy & Huber, 1973); *SHELXS*86, multi-solution program (Sheldrick, 1986); *SHELX*76, program for structure determination (Sheldrick, 1976); and *ORTEP*, stereodrawings (Johnson, 1965).

† Lists of structure factors, anisotropic thermal parameters, bond distances and angles involving H atoms and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54953 (16 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CD0066]
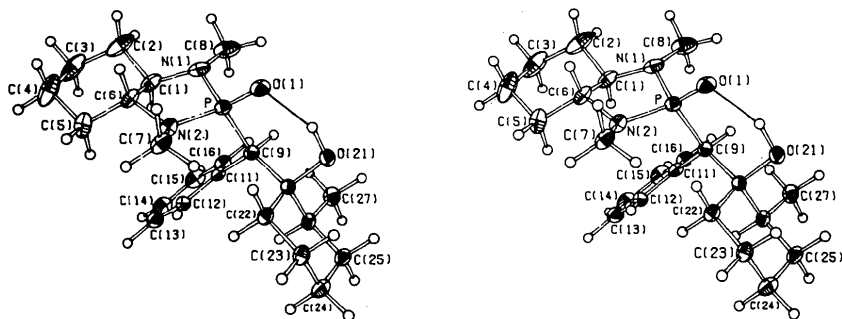
Fig. 1. *ORTEP* view of the $C_{22}H_{35}N_2O_2P$ molecule with the numbering scheme used. Atoms represented at 50% probability level, H atoms with arbitrary spheres.

Table 1. *Final atomic coordinates with their e.s.d.'s* ($\times 10^4$; *for* $P \times 10^5$) *and equivalent isotropic temperature factors* ($\mathring{A}^2 \times 10^3$) *for* $C_{22}H_{35}N_2O_2P$

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
P	93288 (13)	50000	70689 (8)	48
O(1)	9573 (3)	6491 (4)	6561 (2)	62
O(21)	6626 (3)	7268 (4)	6538 (2)	55
N(1)	10393 (4)	4665 (6)	8061 (2)	59
N(2)	9785 (4)	3368 (5)	6527 (2)	48
C(1)	10703 (5)	3020 (7)	8117 (3)	64
C(2)	12050 (5)	2516 (9)	8748 (3)	101
C(3)	12167 (6)	762 (9)	8680 (4)	119
C(4)	12188 (6)	152 (10)	7627 (4)	116
C(5)	10899 (6)	786 (7)	6989 (4)	84
C(6)	10933 (5)	2536 (7)	7092 (3)	59
C(7)	9935 (5)	3313 (8)	5466 (3)	68
C(8)	10242 (6)	5588 (9)	8937 (4)	101
C(9)	7401 (4)	4941 (7)	7433 (3)	41
C(11)	7006 (4)	3442 (6)	7903 (3)	40
C(12)	6907 (4)	2048 (6)	7414 (3)	48
C(13)	6578 (5)	665 (6)	7881 (3)	61
C(14)	6349 (5)	685 (7)	8862 (4)	73
C(15)	6433 (5)	2052 (7)	9356 (3)	70
C(16)	6753 (5)	3414 (6)	8892 (3)	52
C(21)	6290 (4)	5666 (5)	6657 (3)	39
C(22)	6356 (4)	4865 (7)	5671 (3)	49
C(23)	5236 (5)	5485 (6)	4916 (4)	58
C(24)	3699 (5)	5340 (7)	5281 (3)	66
C(25)	3616 (5)	6217 (6)	6236 (3)	59
C(26)	4693 (4)	5584 (6)	7014 (3)	43
C(27)	4496 (5)	6459 (7)	7956 (3)	63

Table 2. *Interatomic distances* ($\mathring{A}$), *angles* (°) *and torsion angles* (°) *with their e.s.d.'s for* $C_{22}H_{35}N_2O_2P$

P—O(1)	1.484 (3)	C(9)—C(21)	1.572 (6)
P—N(1)	1.670 (3)	C(11)—C(12)	1.378 (7)
P—N(2)	1.653 (4)	C(11)—C(16)	1.392 (6)
P—C(9)	1.845 (4)	C(12)—C(13)	1.392 (7)
N(1)—C(1)	1.446 (8)	C(13)—C(14)	1.377 (7)
N(1)—C(8)	1.457 (7)	C(14)—C(15)	1.361 (8)
N(2)—C(6)	1.465 (6)	C(15)—C(16)	1.373 (8)
N(2)—C(7)	1.476 (5)	O(21)—C(21)	1.424 (6)
C(1)—C(2)	1.537 (7)	C(21)—C(22)	1.528 (6)
C(1)—C(6)	1.496 (6)	C(21)—C(26)	1.555 (6)
C(2)—C(3)	1.518 (11)	C(22)—C(23)	1.524 (6)
C(3)—C(4)	1.545 (8)	C(23)—C(24)	1.511 (6)
C(4)—C(5)	1.538 (8)	C(24)—C(25)	1.523 (7)
C(5)—C(6)	1.514 (8)	C(25)—C(26)	1.525 (6)
C(9)—C(11)	1.495 (7)	C(26)—C(27)	1.519 (6)
O(1)—P—N(1)	116.3 (2)	P—C(9)—C(21)	113.4 (3)
O(1)—P—N(2)	118.5 (2)	C(11)—C(9)—C(21)	118.6 (4)
O(1)—P—C(9)	108.3 (2)	C(9)—C(11)—C(12)	123.5 (4)
N(1)—P—N(2)	94.3 (2)	C(9)—C(11)—C(16)	119.4 (4)
N(1)—P—C(9)	107.4 (2)	C(12)—C(11)—C(16)	117.0 (4)
N(2)—P—C(9)	111.0 (2)	C(11)—C(12)—C(13)	122.0 (4)
P—N(1)—C(1)	108.6 (3)	C(12)—C(13)—C(14)	119.2 (4)
P—N(1)—C(8)	121.0 (3)	C(13)—C(14)—C(15)	119.7 (5)
C(1)—N(1)—C(8)	121.0 (4)	C(14)—C(15)—C(16)	121.0 (5)
P—N(2)—C(6)	111.2 (3)	C(11)—C(16)—C(15)	121.2 (4)
P—N(2)—C(7)	120.7 (3)	O(21)—C(21)—C(9)	109.2 (3)
C(6)—N(2)—C(7)	114.8 (4)	O(21)—C(21)—C(22)	108.6 (3)
N(1)—C(1)—C(2)	117.2 (4)	O(21)—C(21)—C(26)	106.8 (3)
N(1)—C(1)—C(6)	104.9 (4)	C(9)—C(21)—C(22)	112.3 (4)
C(2)—C(1)—C(6)	108.5 (4)	C(9)—C(21)—C(26)	110.5 (3)
C(1)—C(2)—C(3)	107.6 (5)	C(22)—C(21)—C(26)	109.4 (4)
C(2)—C(3)—C(4)	113.6 (5)	C(21)—C(22)—C(23)	113.6 (4)
C(3)—C(4)—C(5)	112.3 (5)	C(22)—C(23)—C(24)	110.3 (4)

Table 2 (*cont.*)

C(4)—C(5)—C(6)	106.7 (5)	C(23)—C(24)—C(25)	109.0 (4)
N(2)—C(6)—C(1)	104.0 (4)	C(24)—C(25)—C(26)	112.2 (4)
N(2)—C(6)—C(5)	115.2 (4)	C(21)—C(26)—C(25)	110.1 (4)
C(1)—C(6)—C(5)	111.3 (4)	C(21)—C(26)—C(27)	113.1 (4)
P—C(9)—C(11)	112.9 (3)	C(25)—C(26)—C(27)	109.3 (4)
P—N(1)—C(1)—C(6)	39.3 (4)	P—N(1)—C(1)—C(2)	159.6 (4)
N(1)—C(1)—C(6)—N(2)	-41.4 (5)	P—N(2)—C(6)—C(5)	150.0 (4)
C(1)—C(6)—N(2)—P	27.9 (4)		
C(6)—N(2)—P—N(1)	-5.2 (3)		
N(2)—P—N(1)—C(1)	-20.5 (3)		
C(1)—P—C(2)—C(3)—C(4)	53.7 (6)	O(1)—P—C(9)—C(11)	176.7 (3)
C(2)—C(3)—C(4)—C(5)	-51.9 (7)	O(1)—P—C(9)—C(21)	38.1 (4)
C(3)—C(4)—C(5)—C(6)	52.9 (6)	N(1)—P—C(9)—C(11)	-56.9 (4)
C(4)—C(5)—C(6)—C(1)	-62.4 (6)	N(1)—P—C(9)—C(21)	164.5 (3)
C(5)—C(6)—C(1)—C(2)	68.0 (5)	N(2)—P—C(9)—C(11)	44.9 (4)
C(6)—C(1)—C(2)—C(3)	-60.5 (6)	N(2)—P—C(9)—C(21)	-93.6 (3)
O(1)—P—N(1)—C(1)	-145.4 (3)	C(9)—P—N(1)—C(1)	93.1 (3)
O(1)—P—N(2)—C(6)	118.0 (3)	C(9)—P—N(2)—C(6)	-115.7 (3)
O(1)—P—N(1)—C(8)	68.0 (3)	C(9)—P—N(1)—C(8)	-53.5 (4)
O(1)—P—N(2)—C(7)	-20.9 (4)	C(9)—P—N(2)—C(7)	105.4 (4)

Hydrogen-bonding distances and angles

A—H$\cdots B$	$A\cdots B$ ($\mathring{A}$)	A—H ($\mathring{A}$)	H$\cdots B$ ($\mathring{A}$)	A—H$\cdots B$ (°)
O(21)—HO(21)$\cdots$O(1)	2.763 (4)	0.92 (5)	2.01 (6)	138 (5)

C(21)—O(21)$\cdots$O(1)	88.7 (2)°	C(21)—O(21)$\cdots$HO(21)	118 (4)°
P—O(1)$\cdots$O(21)	92.9 (2)	P—O(1)$\cdots$HO(21)	105 (2)

as observed with electrophiles in previous studies by Hanessian, Delorme, Beaudoin & Leblanc (1984), Bélanger-Gariépy, Delorme, Hanessian & Brisse (1986), Bélanger-Gariépy, Bennani, Hanessian & Brisse (1989), Bennani, Bélanger-Gariépy & Hanessian (1990), Hanessian, Bennani & Delorme (1990) and Bennani & Hanessian (1991).

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